FAST *d-f* LUMINESCENCE OF Pr^{3+} IONS IN SOME COMPLEX PHOSPHATES AND SILICATES: COMPARATIVE CHARACTERISTICS

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It is well known that wide-gap compounds, in particular, complex silicates, phosphates, binary RE halides doped with Ce^{3+} or Pr^{3+} ions, are used as fast scintillation detectors due to their high light yield and fast nanosecond luminescence decay kinetics [1-5]. Our search for novel materials showing fast $5d\rightarrow4f$ emission of Pr^{3+} has led us to the synthesis and spectroscopic investigation of the phosphates $LiSrPO_4$, $Sr_9Sc(PO_4)_7$, $K_3Lu(PO_4)_2$, and silicate $K_3LuSi_2O_7$ doped with this ion.

All samples showed Pr^{3+} emission connected with interconfigurational $4f^15d\rightarrow4f^2$ transitions in the UV range and intraconfigurational $4f^2\rightarrow4f^2$ transitions in VIS-IR region. However, the relative yield of $d\rightarrow f$ and $f\rightarrow f$ emission depends on the exciting photons energy and temperature.

At room temperature, the yield of $d\rightarrow f$ emissions relative to $f\rightarrow f$ emissions upon host excitation (X-ray or cathode rays) is less than upon intra-center photoexcitation. The things are changing with decreasing temperature from 295 to 90 K: the XRL yield of the $d\rightarrow f$ emission decreases (in $LiSrPO_4$ and $K_3Lu(PO_4)_2$) or increases (in $K_3LuSi_2O_7$) by several times. In $Sr_9Sc(PO_4)_7$ the intensity of the broad defect related band at 360 nm increases significantly with decreasing temperature.

Stokes shift for Pr^{3+} $d\rightarrow f$ transitions is presented in table. According to the model for Pr^{3+} emission proposed by Srivastava et al. [2] $d\rightarrow f$ transitions dominate over $f\rightarrow f$ ones when the Stokes shift is lower than 3000 cm^{-1}. Therefore, a large Stokes shift is one of the reasons that both types of radiative transitions are observed in all investigated materials except $K_3Lu(PO_4)_2$, which has faint $f\rightarrow f$ peaks.

Upon cathode rays excitation (E=120 keV, 200 ps, 5 Hz) the decay kinetics of the phosphates $d\rightarrow f$ emission is dominated by a fast component (see table), the value of which is consistent with this parameter observed in the wider phosphate family. The silicate $K_3LuSi_2O_7$ demonstrated the build-up stage (7-12 ns) and longer decays time.

Upon high-frequency (8 MHz) X-ray pulse excitation, the $d\rightarrow f$ emission decay kinetics departs from an exponential behavior and demonstrates the presence of intense slow decay component appearing as a background. Only $Sr_9Sc(PO_4)_7$ reveals a fast component ($\tau\sim15$ ns) while the contribution of the slow μs decay component reaches 18%.

The presence of defects was shown with measurements of thermo-stimulated luminescence and suggested to be the main reason for delayed recombination of charge carriers on Pr^{3+} $4f^15d$ states.

Finally, the luminescence spectroscopic and dynamic properties of investigated materials along with high effective atomic number revealed good potentialities for their application as fast scintillators.

Comparative characteristics of polycrystalline samples doped with Pr^{3+} ion, T= 295 K

Material	$Z_{эфф}$	λ_{max}, nm	τ, ns	Stokes shift, cm^{-1}	d-f/f-f
$Sr_9Sc(PO_4)_7$:Pr (1%)	35.3	265; 300	17	4630	0.01
$LiSrPO_4$:Pr (1%)	34.9	265; 269	18	4230	0.5
$K_3Lu(PO_4)_2$:Pr (1 and 5 %)	64.5	280; 320	15-20	2850	10
$K_3LuSi_2O_7$:Pr (1%)	64.9	284; 330	54	6110	1.4

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LUMINESCENCE OF $Li_6Y(BO_3)_3$ DOPED WITH Pr^{3+} IONS UNDER X-RAY, ELECTRON BEAM AND ULTRAVIOLET EXCITATION

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This paper reports the spectroscopic properties of praseodymium-doped lithium yttrium triple borates, $Li_6Y(BO_3)_3$:Pr^{3+}(1%). Emission and photoluminescence excitation spectra were measured at room temperature in the near IR and VIS-UV range. For this Pr^{3+}- doped triple borates, the interconfigurational $4f^15d \rightarrow 4f^2$ transitions with nanosecond decay time were detected. Besides the intraconfigurational $4f^2 \rightarrow 4f^2$ transitions in visible and near IR regions were analyzed.

Progress in the development of new luminescent materials is directly related to the understanding of the physical processes of energy absorption and relaxation in solids. The $4f^15d \rightarrow 4f^2$ absorption and emission in crystalline hosts is receiving at the present special attention due to the applications in both fast scintillators and ultraviolet (UV) tunable solid-state laser devices.

In the frame of scintillating materials research, a variety of crystalline host and dopant systems are investigated but mainly the Ce^{3+} and Pr^{3+}ions in different host matrices are studied as the most promising materials [1]. However, the knowledge on the spectroscopic properties of such compounds is still limited. In the present report, the Pr^{3+}-doped triple borates are the subject of our studies. A high cross section for the interaction of thermal neutrons with crystal-forming atoms may be promising for the conversion of absorbed energy into a scintillation pulse.